L Number	Hits	Search Text	DB	Time stamp
1	35	gen with kanai	USPAT; EPO; JPO; DERWENT	2003/06/20 11:02
2	109	takao with tayano	USPAT; EPO; JPO; DERWENT	2003/06/20 11:11
3	117	tadashi with sezume	USPAT; EPO; JPO; DERWENT	2003/06/20 11:37
4	749	japan with polychem	USPAT; EPO; JPO; DERWENT	2003/06/20 11:20
5	12	(japan with polychem) and (shrink shrinkable shrinking shrunk) and (label labelling)	USPAT; EPO; JPO; DERWENT	2003/06/20 12:22
6	22	(japan with polychem) and (shrink shrinkable shrinking shrunk)	USPAT; EPO; JPO; DERWENT	2003/06/20 11:45
7	2	(main adj fusion adj peak) and (crystallization crystalline) and (shrink shrinkable shrinking)	USPAT; EPO; JPO; DERWENT	2003/06/20 11:39
8	8	(main adj fusion adj peak) and (crystallization crystalline)	USPAT; EPO; JPO; DERWENT	2003/06/20 11:40
9	3	(main adj fusion adj peak) and (shrink shrinkable shrinking)	USPAT; EPO; JPO; DERWENT	2003/06/20 11:39
10	1	(main adj fusion adj peak) and (nippon adj polychem)	USPAT; EPO; JPO; DERWENT	2003/06/20 11:40
11	11	(main adj fusion adj peak)	USPAT; EPO; JPO; DERWENT	2003/06/20 11:41
12	175	yasunori with nakamura	USPAT; EPO; JPO; DERWENT	2003/06/20 11:41
13	13	(japan with polychem) and (heat with fusion)	USPAT; EPO; JPO; DERWENT	2003/06/20 11:46
14	294	(propylene polypropylene) and (heat with fusion) and (crystalline crystallinity) and (shrink shrinking shrinkable shrunk shrunken)	USPAT; EPO; JPO; DERWENT	2003/06/20 11:49
15	28	(propylene polypropylene) and (heat with fusion) and (crystalline crystallinity) and (shrink shrinking shrinkable shrunk shrunken) and (label labelling labelling)	USPAT; EPO; JPO; DERWENT	2003/06/20 11:51
16	10	((propylene polypropylene) same (crystalline crystallinity)) and (shrink shrinking shrinkable shrunk shrunken) and (label labelling labelling) and (heat with fusion)	USPAT; EPO; JPO; DERWENT	2003/06/20 11:51
17	6	(japan with polychem) and (softening adj temperature)	USPAT; EPO; JPO; DERWENT	2003/06/20 12:22

23	19	"5594070"	USPAT; EPO; JPO; DERWENT	2003/06/20 12:55
24	89	428/34.9 and ((polypropylene propylene) with (crystalline crystallinity))	USPAT; EPO; JPO; DERWENT	2003/06/20 12:58
25	19	428/34.9 and ((polypropylene propylene) with (crystalline crystallinity)) and (label labelling)	USPAT; EPO; JPO; DERWENT	2003/06/20 13:09
26	26	"126640"	USPAT; EPO; JPO; DERWENT	2003/06/20 13:09
27	39	((propylene polypropylene) same (crystalline crystallinity)) and (shrink shrinking shrinkable shrunk shrunken) and (label labelling labelling) and ((glass adj transition) (softening adj temperature))	USPAT; EPO; JPO; DERWENT	2003/06/20 13:13

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10	1	(main adj fusion adj peak) and (nippon adj polychem)	USPAT; EPO; JPO; DERWENT	2003/06/20 11:40
11	11	(main adj fusion adj peak)	USPAT; EPO; JPO; DERWENT	2003/06/20 11:41
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16	10	((propylene polypropylene) same (crystalline crystallinity)) and (shrink shrinking shrinkable shrunk shrunken) and (label labelling labelling) and (heat with fusion)	USPAT; EPO; JPO; DERWENT	2003/06/20 13:12
17	6	(japan with polychem) and (softening adj temperature)	USPAT; EPO; JPO; DERWENT	2003/06/20 12:22
18	2	"6469100"	USPAT; EPO; JPO; DERWENT	2003/06/20 12:33
19	11	"4592960"	USPAT; EPO; JPO; DERWENT	2003/06/20 12:34
20	18	"4528329"	USPAT; EPO; JPO; DERWENT	2003/06/20 12:34
21	0	softening and (yasunori with nakamura)	USPAT; EPO; JPO; DERWENT	2003/06/20 12:50
22	0	(glass adj transition) and (yasunori with nakamura)	USPAT; EPO; JPO; DERWENT	2003/06/20 12:50

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28	348	((propylene polypropylene) same (crystalline crystallinity)) and (shrink shrinking shrinkable shrunk shrunken) and ((glass adj transition) (softening adj temperature))	USPAT; EPO; JPO; DERWENT	2003/06/20 13:30
29	23	hiroki with ogawa	USPAT; EPO; JPO; DERWENT	2003/06/20 13:31
30	15	((propylene polypropylene) same (crystalline crystallinity)) and (shrink shrinking shrinkable shrunk shrunken) and (label labelling labelling) and (softening adj point)	USPAT; EPO; JPO; DERWENT	2003/06/20 13:34

PATENT ABSTRACTS OF JAPAN

(11)Publication number : **11-335500**
(43)Date of publication of application : **07.12.1999**

(51)Int.Cl. C08L 23/14
C08J 5/18
C08K 3/34
C08K 7/18
// B29C 55/04
B29K 23:00
B29L 7:00

(21)Application number : **11-080535**
(22)Date of filing : **24.03.1999**

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(30)Priority
Priority number : **10 75661** Priority date : **24.03.1998** Priority country : **JP**

(54) PROPYLENE-BASED RESIN COMPOSITION AND DRAWN FILM USING THE SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain the subject composition capable of forming a film for shrink wrapping having excellent low-temperature shrink properties, transparency, luster, blocking resistance, plastic properties, etc., by blending a specific propylene-based resin with a prescribed nucleating agent and a specified anti- blocking agent.
SOLUTION: This composition comprises (A) a propylene/α-olefin random copolymer consisting essentially of propylene having 1-20 g/10 minutes melt flow rate, 130-150°C melt peak temperature by a differential scanning calorimeter, ≤4 wt.% extracted amount in orthodichlorobenzene at 40°C and the ratio of weight-average molecular weight to number-average molecular weight of 1.5-7, (B) a nucleating agent for satisfying the equation 50≤ [A]-[B]≤500 {[A] and [B] are isothermal crystallization times (second) at 115°C before and after the addition of a nucleating agent, respectively} and (C) 0.01-1 pt.wt. based on 100 pts.wt. of the component A of spherical particles of magnesium silicate having 0.5-7 μm average particle diameter and ≥0.7 sphericity.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

* NOTICES *

1. This document has been translated by computer.So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the oriented film which used a propylene system resin constituent and it. In detail, without spoiling low-temperature shrinkage characteristics, it excels in transparency, gloss, and a blocking resistance, and, moreover, excels in the hot slip nature at the time of packing, and the pinhole-proof nature at the time of the shrink package after carrying out a fusing seal, and there are few falls of the transparency after contraction and gloss, and it is further related with the propylene system resin film for shrink packages without defluxion of the anti blocking agent in the time of film production, or a slit.
[0002]
[Description of the Prior Art] Conventionally, although the polypropylene film was widely used for 2 shaft orientations by packing of instant food containers, such as a rahmen and an alcohol pack, as a shrink film with shrinkage characteristics, it was not what has not necessarily satisfied the above-mentioned quality. For example, in order to obtain the outstanding film of low-temperature shrinkage characteristics. Although the method of increasing the ethylene content in a propylene ethylene random copolymer, lowering dissolution peak temperature, and improving low-temperature shrinkage characteristics is proposed The method of increasing this ethylene content A blocking resistance, scratch-proof nature, the hot slip nature at the time of packing (the slip nature in the process (heated at the heater of a fusing seal) which inserts in a film on a tube by the shrink wrapping machine, and packs a container --) Or there was a problem that a container comrade's (at boxed process) slip nature by which shrink packing was carried out, the pinhole-proof nature at the time of the shrink package after carrying out a fusing seal, the transparency after contraction, or gloss fell immediately after shrink tunnel passage. Moreover, there was a problem that powder is generated during film production at the time of the dusting arrival to the roll top by defluxion of an anti blocking agent though such quality is satisfied, and a slit or bag manufacture processing.
[0003]
[Problem(s) to be Solved by the Invention] This invention persons are excellent in transparency, gloss, a blocking resistance, and scratch nature, moreover are excellent in the hot slip nature at the time of packing, and the pinhole-proof nature at the time of the shrink package behind a fusing seal, without spoiling low-temperature shrinkage characteristics in view of the above-mentioned trouble, have few falls of the transparency after contraction, and gloss, and are to offer the propylene system resin film for shrink packages without defluxion of the anti blocking agent in the time of film production, or a slit.
[0004]
[Means for Solving the Problem] this invention is a book by blending a specific nucleating additive and a specific specific anti blocking agent with a specific propylene system resin, as a result of inquiring wholeheartedly, in order to solve this technical problem. Namely, the propylene system resin constituent of this invention To the propylene and alpha olefin random copolymer made into a principal component,

the propylene with which are satisfied of following copolymer property (1) - (4) While making 115-degree-C isothermal crystallization time at the time of adding a nucleating additive [B] into within the limits expressed with a following formula [I] and a following formula [II] To this propylene and alpha olefin random-copolymer 100 weight section, a mean particle diameter carries out 0.5-7.0 micrometers, sphericity (f) carries out 0.01-1 weight section combination of the 0.7 or more magnesium-silicate spherical particles, and it is characterized by the bird clapper.
(**) Copolymer property (1): Melt flow rates are 1.0-20.0g / 10 minutes, (2) : The dissolution peak temperature for which it asked with the differential scan type calorimeter (DSC) is 130-150 degrees C, (3) : The amount of extraction extracted in 40 degrees C by using orthochromatic dichlorobenzene as a solvent is 4.0 or less % of the weight, (4) : That the ratios of the weight average molecular weight and number average molecular weight which were calculated by the gel permeation chromatography (GPC) are 1.5-7.0, (b) 115-degree-C isothermal crystallization time 50 <=[A]-[B] <=500 Formula [I]
[B] <=100 Formula [II]
(Among a formula, [A] expresses 115-degree-C isothermal crystallization time (second) found by DCS of the propylene and alpha olefin random copolymer before nucleating additive addition, and [B] expresses 115-degree-C isothermal crystallization time (second) found by DCS of the propylene and alpha olefin random copolymer after nucleating additive addition.)
[0005] Moreover, the oriented film which is another invention of this invention To the propylene and alpha olefin random copolymer made into a principal component, the propylene with which are satisfied of following copolymer property (1) - (4) While making 115-degree-C isothermal crystallization time at the time of adding a nucleating additive [B] into within the limits expressed with a following formula [I] and a following formula [II] As opposed to this propylene and alpha olefin random-copolymer 100 weight section After producing the propylene system resin constituent with which the mean particle diameter carried out 0.5-7.0 micrometers, and sphericity (f) carried out 0.01-1 weight section combination of the 0.7 or more magnesium-silicate spherical particles a sheet or in the shape of a film, it extends to at least 1 shaft orientations, and is characterized by the bird clapper.
(**) Copolymer property (1): Melt flow rates are 1.0-20.0g / 10 minutes, (2) : The dissolution peak temperature for which it asked with the differential scan type calorimeter (DSC) is 130-150 degrees C, (3) : The amount of extraction extracted in 40 degrees C by using orthochromatic dichlorobenzene as a solvent is 4.0 or less % of the weight, (4) : That the ratios of the weight average molecular weight and number average molecular weight which were calculated by the gel permeation chromatography (GPC) are 1.5-7.0, (b) 115-degree-C isothermal crystallization time 50 <=[A]-[B] <=500 Formula [I]
[B] <=100 Formula [II]
(Among a formula, [A] expresses 115-degree-C isothermal crystallization time (second) found by DCS of the propylene and alpha olefin random copolymer before nucleating additive addition, and [B] expresses 115-degree-C isothermal crystallization time (second) found by DCS of the propylene and alpha olefin random copolymer after nucleating additive addition.)
[0006]
[Embodiments of the Invention] [I] Propylene system resin constituent (1) Constituent (A) The propylene and alpha olefin random copolymer which made the principal component the propylene used in the propylene system resin constituent of a propylene and an alpha olefin random-copolymer this invention The propylene of a principal component, the carbon number 2 of an accessory constituent, or 4-20 -- preferably, it is a random copolymer with the alpha olefin of 4-8 preferably, and they are the alpha olefin of 4-8 or ethylene and carbon numbers 4-20, and the thing that satisfies following copolymer property (1) - (4)
[0007] (**) copolymer property (1): a melt flow rate (MFR:Melt Flow Rate) -- 1.0-20.0g/-- it is within the limits of 1.0-10.0g / 10 minutes preferably for 10 minutes When a melt flow rate is under the above-mentioned range, the extrusion-molding nature of a film becomes poor. On the other hand, when exceeding the above-mentioned range, the impact strength of a film falls remarkably.
[0008] (2): 130-150 degrees C of temperature of the dissolution peak searched for with the differential

scan type calorimeter (DSC:Differential Scanning Calorimeter) should be within the limits of 130-145 degrees C preferably. In the case of the propylene and alpha olefin random copolymer which made the propylene the principal component, dissolution peak temperature is changed with how, and its content. [the regularity of a propylene segment, the kind of comonomer, and a comonomer] for example, -- although the support support type catalyst mentioned later is depended also on how by the copolymer of the propylene made into the catalyst, and ethylene -- an ethylene content -- 2.9-8.7-mol % -- dissolution peak temperature serves as the above-mentioned range by about 4.4-8.7 mol % preferably [ethylene] When the dissolution peak temperature for which it asked with the differential scan type calorimeter is under the above-mentioned range, a blocking resistance and scratch nature get worse. On the other hand, when exceeding the above-mentioned range, defluxion of an anti blocking agent arises, or shock resistance falls.

[0009] (3): The amount of extraction which used orthochromatic dichlorobenzene as a solvent and was extracted in 40 degrees C should be 2.0 or less % of the weight preferably 4.0 or less % of the weight. Although especially a process will not be limited if it is in the above-mentioned range, the method of using the catalyst system which used the support support type catalyst component and the electron-donative compound, the method of washing the polymer which obtained as a catalyst the catalyst component which contains a titanium trichloride or a titanium trichloride as a principal component, etc. are mentioned. Orthochromatic dichlorobenzene is used as a solvent, and if the amount of extraction extracted in 40 degrees C exceeds the above-mentioned range, the transparency after contraction, gloss, and scratch nature will fall. The extraction by orthochromatic dichlorobenzene can be measured by temperature rise elution judgment (TREF:Temperature Rising Elution Fractionation) which used orthochromatic dichlorobenzene as the solvent.

Measurement of the temperature rise elution judgment (TREF) TREF is Journal. of Applied PolymerScience The 26th volume It can carry [page / 4217-4231st / (1981)] out by the equipment and the method of a publication.

[0010] (4): the ratio (molecular weight distribution) of the weight average molecular weight and number average molecular weight which were calculated by the gel permeation chromatography (GPC) -- 1.5-7.0 -- it is within the limits of 2.0-6.0 preferably When molecular weight distribution are under the above-mentioned ranges, extrusion-molding nature becomes poor, and when exceeding the above-mentioned range, the transparency of a film falls.

(a) Seed A kind as the propylene and an alpha olefin random copolymer which made the principal component the propylene to apply for example, the duality of the propylene which made the propylene the principal component, and other 1-alkenes (ethylene, 1-butene, 1-pentene, 1-hexene, 4-methyl pentene-1 grade) -- a copolymer -- Or the ternary polymerization object of the propylene and ethylene which made the propylene the principal component, and other 1-alkenes (1-butene, 1-pentene, 1-hexene, 4-methyl pentene-1 grade) etc. can be mentioned.

[0011] (b) ** The propylene and alpha olefin random copolymer which made the principal component ** or the propylene to cut can be manufactured with the application of the conventional well-known manufacture method.

** intermediation -- especially as a catalyst used for manufacture of these, although not restricted, the catalyst of the metallocene system called Kaminsky catalyst can also be used, for example Moreover, the catalyst system which contains a titanium content solid-state catalyst component and an organoaluminium compound as a cocatalyst component can be mentioned. It is chosen out of the well-known catalyst component which contains the well-known support support type catalyst component, titanium trichloride, or titanium trichloride which a magnesium compound, solid 4 halogenation titanium, and a solid electron-donative compound are contacted, and is obtained as this titanium content solid-state catalyst component as a principal component. Furthermore, you may use the catalyst system which used the electron-donative compound well-known as the third component other than the above-mentioned solid-state catalyst component and a cocatalyst component.

[0012] Pile A ****** format can take all formats, if a catalyst component and each monomer contact

efficiently. Specifically, bulk pile lawfulness and a solution polymerization method using a propylene as a solvent, or the vapor-phase-polymerization method which keeps each monomer substantial in the shape of gas not using a liquid solvent substantially is employable, not using substantially the slurry polymerization method and inert solvent using an inert solvent. Moreover, it is applied also to a continuation polymerization and a batch-process polymerization. In the case of a slurry polymerization, saturated-fat groups, such as a hexane, a heptane, a pentane, a cyclohexane, benzene, and toluene, or independent or mixture of an aromatic hydrocarbon is used as a polymerization solvent.

[0013] (B) Nucleus The nucleating additive used in the propylene system resin constituent of an agent this invention If the following formula [I] and a formula [II] are filled by the use The 3-methylbutene -1, aluminum hydroxy-G parlor t-butyl benzoate which are an organic system nucleating additive although there are especially no restrictions in the kind and addition, A JIBEN zylidene sorbitol, a dimethyl benzylidene sorbitol, A screw (2, 4, 8, 10-tetrapod-t-butyl-6-hydroxy-12H-dibenzo [d, g] [1, 3, 2] dioxa-phosphocin-6-oxide) aluminum-hydroxide salt, Phosphoric acid -2, 2-methylene screw (4, 6-G t-buthylphenyl) sodium, the talc that is an inorganic system nucleating additive can be mentioned. If phosphoric acid -2 and 2-methylene screw (4, 6-G t-buthylphenyl) sodium are especially used also in these nucleating additives, since the effect is remarkable also at a little addition, it is desirable.

[0014] When the above-mentioned nucleating additive is added to the propylene and alpha olefin random copolymer which makes the aforementioned propylene a principal component, 115-degree-C isothermal crystallization time [B] by measurement of the differential scan type calorimeter (DSC) of the propylene and alpha olefin random copolymer which makes this propylene a principal component is within the limits expressed with a following formula [I] and a following formula [II].

Formula [I]

$50 \leq [A]-[B] \leq 500$ formula [II]

$[B] \leq 100$ (however, [A] in a formula expresses 115-degree-C isothermal crystallization time (second) found by DSC of the propylene and alpha olefin random copolymer before nucleating additive addition, and [B] expresses 115-degree-C isothermal crystallization time (second) found by DSC of the propylene and alpha olefin random copolymer after nucleating additive addition.)

If a moldability and scratch nature become poor for 115 degree-C isothermal crystallization [time A]-[B] to be under the range of the above-mentioned formula [I] and the range is exceeded on the other hand, pinhole-proof nature will become poor. Moreover, if [B] exceeds the range of the above-mentioned formula [II], scratch nature and pinhole-proof nature will become poor.

After taking the amount of samples of 5.0mg and holding for 5 minutes at 200 degrees C using DSC by isothermal (115 degrees C) crystallization time-measurement SEIKO CORP. by the differential scan type calorimeter (DSC), it lowers the temperature and holds to 115 degrees C at 40-degree-C speed for /. It asks by measuring between the crystallization peak periods after a hold (second) (unit : second).

[0015] (C) As a magnesium-silicate spherical particle used for the propylene system resin constituent of a magnesium-silicate spherical particle this invention, a mean particle diameter is 0.5-7.0 micrometers, and sphericity is 0.7 or more things, and when the empirical formula is shown (SiO_2), it is x-(MgO) -(Na_2O) z-(H_2O) n, and is the $x+y+z+n=100$ % of the weight in a formula. This magnesium silicate is obtained by making the silicon dioxide (SiO_2) and magnesium hydroxide ($Mg_2(OH)$) which were produced by the gel method react, and commercial elegance can also be used for it.

(a) As for a mean-particle-diameter mean particle diameter, 0.5-7 micrometers of 1.0-5.0-micrometer things are used preferably. There is an inclination to roll round if there is an inclination for the transparency of the film which will be obtained if a mean particle diameter uses the thing exceeding the above-mentioned range to fall and the thing of under the above-mentioned range is used, and for the slipping nature and the blocking resistance of a film at the time to fall.

The mean particle diameter of the magnesium-silicate spherical impalpable powder used in the measurement this invention of a mean particle diameter is measured by the Coulter-counter method.

[0016] (b) Sphericity (f)

0.8 or more things are preferably used for the sphericity (f) asked for the magnesium-silicate spherical

particle used in this invention by the following formula 0.7 or more.
[0017]
[Equation 1]
$$f = \sqrt{A / (\pi / 4)} \times Dmax$$

[0018] (Here, A is the cross section (mm2) of a particle, Dmax is the diameter of the longest of this cross section (mm), the ranges of ** of the sphericity given by this formula are 0-1, and a true sphere is 1.)
The slipping nature of the film which will be obtained if sphericity (f) uses the thing of under the above-mentioned range gets worse.
Measurement of the measurement sphericity (f) of sphericity (f) is called for by measuring the cross section (mm2) of a particle, and the diameter of the longest of this cross section (mm). Concrete measurement adds an epoxy resin to the spherical particle of a magnesium silicate, solidifies to it, is cut with a microtome, and is performed by measuring the cross section of a particle with an image analyzer.
[0019] (2) amount the propylene and the alpha olefin random-copolymer 100 weight section to which the loadings of the ratio above-mentioned magnesium-silicate spherical particle made the propylene the principal component -- receiving -- the 0.01 - 1.0 weight section -- desirable -- the 0.05 - 0.6 weight section -- especially, the 0.1 - 0.4 weight section comes out comparatively preferably, and it blends Since generating of a fish eye and aggravation of transparency will be caused if the improvement effects of the slipping nature of the film with which loadings are obtained under in the above-mentioned range, and a blocking resistance run short and loadings exceed the above-mentioned range, it is not desirable.
[0020] [II] As a method of manufacturing the propylene system resin constituent of the manufacture this invention of a constituent The above-mentioned nucleating additive and a spherical anti blocking agent are blended with the propylene and alpha olefin random copolymer which makes a propylene a principal component. Although which method may be used as long as it is the method which these components distribute and mix uniformly After measuring each for various additives by making powdered propylene and alpha olefin random copolymer into a principal component, It is desirable for a ribbon blender, a Henschel mixer, etc. to be sufficient, and to mix and carry out uniform distribution, while it has been powdered, to cool, to cut the powdered mixture, after carrying out melting kneading using screw extruders, such as a single screw extruder and a twin screw extruder, etc., and especially to use as pellet-like mixture. In addition, it is also possible to make it the combination range which creates the pellet-like compound which blended the above-mentioned nucleating additive and the anti blocking agent of a true spherical with high concentration in masterbatch, mixes the pellet-like compound blended with high concentration in this masterbatch at the time of film manufacture and a non-added pellet, and is used by this invention, and to film-ize.
Well-known additives, such as an antioxidant, a slipping agent, a neutralizer, an antistatic agent, a weathering agent, an antifogger, a pigment, and a filler, can be made to contain in propylene system resin constituents of the aforementioned this invention, such as an additive, if needed.
[0021] [III] Oriented film (1) The oriented film of the manufacture this invention of an oriented film can be manufactured by the method of manufacturing the usual oriented film, and the same method, using the above-mentioned propylene system resin constituent as a raw material resin. It can obtain by extending to at least 1 shaft orientations by specifically adopting the extension methods, such as the method used for manufacture of the usual industrial oriented film, for example, roll extension, tenter extension, tubular extension, and a pantographic desk drawing machine. In addition, in the case of biaxial stretching, any method of simultaneous, serial, or multi-stage extension is applicable in the two directions. Generally on the other hand, the extension direction is a 3.0 to 10 times as many range as this preferably 2.0 to 12 times to **, and, generally let preferably 5-200 micrometers of thickness of the film after being extended be the range of 8-100 micrometers.
(2) After after treatment and extension, it is common tonus-ization or to heat-treat, easing several%, and it may carry out surface treatment, such as corona discharge, in air or inert gas after that as occasion demands.

[0022]
[Example] this invention is not limited by these examples although the example and the example of comparison which are shown below explain this invention still in detail.
The [evaluation method] In addition, the evaluation method of the film made in the example and the example of comparison is shown below.
(1) It asked for dissolution peak temperature from the curve drawn when it makes it crystallize at 10-degree-C temperature fall speed for /to 40 degrees C and is made to dissolve at 10 more degree-C temperature up speed for /, after taking the amount of samples of 5.0mg and holding for 5 minutes at 200 degrees C using DSC by dissolution peak temperature SEIKO CORP. by the differential scan type calorimeter (DSC) (unit : degree C).
(2) Lower the temperature and hold to 115 degrees C at 40-degree-C speed for /after taking the amount of samples of 5.0mg and holding for 5 minutes at 200 degrees C using DSC by isothermal (115 degrees C) crystallization time SEIKO CORP. by the differential scan type calorimeter (DSC). Between the crystallization peak periods after a hold (second) is measured (unit : second).
(3) Amount equipment of 40-degree-C extraction by temperature rise elution judgment (TREF) : Mitsubishi Chemical make CFC T150A type column : Showa Denko K.K. make AD80 M/S 3 concentration : 40mg / 10ml solvent : Orthochromatic dichlorobenzene. [0023] (4) The ratio of weight average molecular weight and number average molecular weight (molecular weight distribution) Equipment : Made in Waters GPC 150C type column : Showa Denko K.K. make AD80 M/S 3 measurement temperature: 140-degree-C concentration : 20mg / 10ml solvent : Orthochromatic dichlorobenzene (5) Melt flow rate (MFR)
It measured according to the melt flow rate (conditions : 230 degrees C, a load 2.16 kgf) of the polypropylene test method of JIS-K6758 (unit : g / 10 minutes).
(6) Measure MD when the film test piece of 5cm angle of heating contractions being immersed for 10 seconds during the glycerol bath of predetermined temperature, and the contraction of TD.
8% or more, at 100 degrees C, 15% or more, if contraction (%) =(size after size-heating before heating) (size before /heating) x100 contraction is 40% or more, it will judge [80 degrees C] that it is good by 120 degrees C.
[0024] (7) Overcast Degree (Hayes)
Based on ASTM-D1003, the obtained film was measured in the hazemeter. If the Hayes value is low, it means that transparency is excellent. If Hayes is 4.0% or less, it will be judged that it is good.
(8) Gloss (gross)
Based on JIS-Z8741, the obtained film was measured in the gloss meter. If a gross is high, it means that gloss is excellent. If a gross is 120% or more, it will judge that it is good.
(9) Transparency after contraction (Hayes), gloss (gross)
The bag containing a case was created by inserting the commercial videotape containing a case (25mm in width-of-face [of 100mm] x length [of 200mm] x thickness) between two films which were able to be obtained, and carrying out the fusing seal of the film comrade around this case at 230 degrees C (it sets in the in-every-direction direction of a case, and the obtained bag is a rectangle large 15% respectively from a case). The shrink tunnel was made to let pass and carry out shrink of the obtained bag, and the film was stuck in the case. The degree of overcast and gloss of this film were measured. The degree of tunnel inside installation constant temperature was performed in 160 degrees C, and heating time (tunnel pass time) 10 seconds. At 4.0% or less, Hayes after contraction will judge that it is good, if the difference of Hayes before contraction and Hayes after contraction is 0.5% or less. At 120% or more, the gross after contraction will judge that it is good, if the difference of the gross before contraction and the gross after contraction is 10% or less.
[0025] (10) The same side comrade of a blocking nature 2cm(width of face) x15cm (merit) sample film. After piling up covering a length of 5cm, carrying out state adjustment under atmosphere with a temperature of 40 degrees C under the load of 100 g/cm2 for 24 hours and adjusting to the temperature of 23 degrees C enough except for a load, the force which opens a tension tester and shearing exfoliation

of a sample takes at 200mm speed for /was searched for (unit : g/10cm 2). A blocking resistance is so good that this numeric value is small. If it is less than [10cm] 1,000g / 2, a blocking resistance will judge that it is good.
(11) Hot slip nature (unit : coefficient of sliding friction)
The coefficient of static friction measured by the method set to ASTM-D 1894-63 in the thermostatic chamber of 50 degrees C of ambient temperature, 55 degrees C, 60 degrees C, and 65% of relative humidity RH shows. With [hot slip nature] 1.0 [or less], it judges [50 degrees C] that it is good by 0.6 or less and 60 degrees C at 0.4 or less and 55 degrees C.
[0026] (12) Completely like the pinhole-proof nature above-mentioned item at the time of a fusing seal (9), and (Hayes after contraction), the bag containing a videotape case was created and the shrink test was performed. The shrink test was performed with the test number 20. When two or more pieces or three or more holes smaller than 2mm had a hole 2mm or more in the seal section of the film package after shrink, it regarded as a defective, and the following judgments were carried out.
Judgment O: To the whole test number, if the rate of an excellent article is 80% or more, pinhole-proof nature is good judging **. : Receive the whole test number. If the rate of an excellent article is less than 80% at 60% or more, pinhole-proof nature is so so good judging x. : As opposed to the whole test number if the rate of an excellent article is less than 60% -- pinhole-proof nature -- defect (13) The omission profit **** pellet-like resin constituent of an anti blocking agent is quenched at the resin temperature of 240 degrees C with an extruder at melting extrusion and a 40-degree C cooling roller. It considered as the sheet with a thickness of 0.8mm, and tenter formula serial biaxial-stretching equipment was performed this sheet to lengthwise, extension was succeedingly performed in the longitudinal direction 10 times 4 times, and the 20-micrometer film was rolled round for 10 minutes to the paper tube by part for 50m/in taking over speed. Twisted the felt around the roll of this side rolled round to a paper tube, fixed to it, the film was made to grind against a constant pressure, and generating (omission of an anti blocking agent) of powder was checked visually.
(14) On the felt layer of the measurement base which carried out the laminating of the felt to the scratch-proof nature plate, lay the film (touch area : a width-of-face [of 60mm] x length of 60mm) of one more sheet to which the 3.2kg load was applied on this film for measurement, and, on the other hand, slide ** on this film 3 times, after fixing the film for measurement (a width-of-face [of 60mm] x length of 500mm). It observed with [of the film for measurement of the side fixed to felt] the blemish visually, and the result was judged on the following criteria.
O : a blemish is not attached.
x: It has the line-like blemish clearly.
[0027] Let the dissolution peak temperature of 140.5 degrees C and orthochromatic dichlorobenzene for which it asked by ethylene content % and DSC of 5.8 mols be a solvent for example 1 [manufacture of constituent] melt-flow-rate (MFR) 2.3g / 10 minutes. The amount of extraction which was used and was extracted by TREF in 40 degrees C 0.6 % of the weight, As opposed to the nucleating additive additive-free propylene ethylene random-copolymer 100 weight section which 115-degree-C isothermal crystallization time which the ratio of the weight average molecular weight and number average molecular weight which were calculated by GPC found by 5.0 and DSC becomes from 217 seconds As a stabilizer tetrakis [methylene-3-(3', 5'-G t-butyl-4-hydroxyphenyl) propionate] methane The 0.05 weight section, Tris-(2, 4-G t-buthylphenyl) phosphite The 0.05 weight section, As a neutralizer a calcium stearate as the 0.1 weight section and an anti blocking agent 2.0 micrometers of mean particle diameters, To that to which sphericity (f) added oleic amide for the magnesium silicate of 0.90, and added the 0.05 weight section for the 0.05 weight section and the erucic-acid amide as the 0.25 weight section and lubricant After carrying out high-speed mixture of what carried out proper quantity combination of phosphoric acid -2 and the 2-methylene screw (4, 6-G t-buthylphenyl) sodium as a nucleating additive at a room temperature for 1 minute by the Henschel mixer so that 115-degree-C isothermal crystallization time found by DSC may become 15 seconds, With 50mmphi extruder, it fused at 230 degrees C, kneaded, cooled and cut, and the pellet-like propylene system resin constituent was obtained.

[0028] [manufacture of an oriented film] -- using this resin constituent, the 300-micrometer sheet was obtained by the pressing method, and the sheet of 90mm angle was extracted and the biaxially oriented film was obtained on condition that the following
drawing machine : -- desk biaxial-stretching machine temperature made from an Oriental energy machine : 140-degree-C remaining-heat time: -- draw magnification during 2 minutes: -- 4.5 times as many MD as this and the evaluation result of a film with a thickness of about 15 micrometers obtained by the above-mentioned method by 4.5 times many TD [as this] extension speed:10m/are shown in Table 1
[0029] In example 2 example 1, it carried out like the example 1 except having changed the addition of an anti blocking agent into the 0.15 weight section. The evaluation result of the obtained film is shown in Table 1.
[0030] In example 3 example 1, it carried out like the example 1 except having changed the addition of an anti blocking agent into the 0.50 weight section. The evaluation result of the obtained film is shown in Table 1.
[0031] In example 4 example 1, the dissolution peak temperature for which the melt flow rate (MFR) asked by ethylene content % and DSC of 7.5 mols for 2.3g / 10 minutes should use 133.0 degrees C and orthochromatic dichlorobenzene as a solvent. It was used and the ratio of the weight average molecular weight and number average molecular weight which the amount of extraction extracted by TREF in 40 degrees C calculated by GPC 1.5% of the weight carried out like the example 1 except having used 5.6 and the nucleating additive additive-free propylene ethylene random copolymer which 115-degree-C isothermal crystallization time found by DSC becomes from 484 seconds. The evaluation result of the obtained film is shown in Table 1.
[0032] In example 5 example 1, the dissolution peak temperature for which it asked by ethylene content % and DSC of 4.4 mols should use 145.0 degrees C and orthochromatic dichlorobenzene as a solvent for melt-flow-rate (MFR) 2.3g / 10 minutes. It was used and the ratio of the weight average molecular weight and number average molecular weight which the amount of extraction extracted by TREF in 40 degrees C calculated by GPC 0.5% of the weight carried out like the example 1 except having used 4.9 and the nucleating additive additive-free propylene ethylene random copolymer which 115-degree-C isothermal crystallization time found by DSC becomes from 187 seconds. The evaluation result of the obtained film is shown in Table 1.
[0033] In example of comparison 1 example 1, it carried out like the example 1 except having changed the sphericity (f) of an anti blocking agent into 0.55. The evaluation result of the obtained film is shown in Table 2.
[0034] In example of comparison 2 example 1, it carried out like the example 1 except having changed the anti blocking agent into additive-free. The evaluation result of the obtained film is shown in Table 2.
[0035] In example of comparison 3 example 1, it carried out like the example 1 except having changed the anti blocking agent into the indeterminate form silica. The evaluation result of the obtained film is shown in Table 2.
[0036] In example of comparison 4 example 1, except that sphericity (f) changed the anti blocking agent into the poly methyl silsesquioxane of 0.90, it carried out like the example 1. The evaluation result of the obtained film is shown in Table 2.
[0037] In example of comparison 5 example 1, the dissolution peak temperature for which the melt flow rate (MFR) asked by ethylene content % and DSC of 9.5 mols for 2.3g / 10 minutes should use 126.0 degrees C and orthochromatic dichlorobenzene as a solvent. It was used and the ratio of the weight average molecular weight and number average molecular weight which the amount of extraction extracted by TREF in 40 degrees C calculated by GPC 4.0% of the weight carried out like the example 1 except having used 5.9 and the nucleating additive additive-free propylene ethylene random copolymer which 115-degree-C isothermal crystallization time found by DSC becomes from 575 seconds. The evaluation result of the obtained film is shown in Table 2.
[0038] In example of comparison 6 example 1, the dissolution peak temperature for which the ethylene

content asked [the melt flow rate (MFR)] by 2.7-mol % and DSC for 2.3g / 10 minutes should use 152.0 degrees C and orthochromatic dichlorobenzene as a solvent. It was used and the ratio of the weight average molecular weight and number average molecular weight which the amount of extraction extracted by TREF in 40 degrees C calculated by GPC 0.5% of the weight carried out like the example 1 except having used 4.9 and the nucleating additive additive-free propylene ethylene random copolymer which 115-degree-C isothermal crystallization time found by DSC becomes from 100 seconds. The evaluation result of the obtained film is shown in Table 3.

[0039] In example of comparison 7 example 1, the dissolution peak temperature for which the ethylene content asked [the melt flow rate (MFR)] by 5.8-mol % and DSC for 2.3g / 10 minutes should use 140.5 degrees C and orthochromatic dichlorobenzene as a solvent. It was used and the ratio of the weight average molecular weight and number average molecular weight which the amount of extraction extracted by TREF in 40 degrees C calculated by GPC 5.5% of the weight carried out like the example 1 except having used 5.7 and the nucleating additive additive-free propylene ethylene random copolymer which 115-degree-C isothermal crystallization time found by DSC becomes from 297 seconds. The evaluation result of the obtained film is shown in Table 3.

[0040] In example of comparison 8 example 1, the dissolution peak temperature for which the ethylene content asked [the melt flow rate (MFR)] by 6.0-mol % and DSC for 2.3g / 10 minutes should use 139.0 degrees C and orthochromatic dichlorobenzene as a solvent. It was used and the ratio of the weight average molecular weight and number average molecular weight which the amount of extraction extracted by TREF in 40 degrees C calculated by GPC 3.9% of the weight carried out like the example 1 except having used 7.2 and the nucleating additive additive-free propylene ethylene random copolymer which 115-degree-C isothermal crystallization time found by DSC becomes from 344 seconds. The evaluation result of the obtained film is shown in Table 3.

[0041] In example of comparison 9 example 1, the nucleating additive (3-methylbutene -1) was performed like the example 1 except having carried out optimum dose combination so that 115-degree-C isothermal crystallization time found by DSC might become 170 seconds. The evaluation result of the obtained film is shown in Table 3.

[0042] In example of comparison 10 example 1, it carried out like the example 1 except having made the nucleating additive additive-free. The evaluation result of the obtained film is shown in Table 3.

[0043] In six to example 10 example 1, it carried out like the example 1 except having changed the kind of nucleating additive into the following compound. The evaluation result of the obtained film is shown in Table 4.

example 6:3-methylbutene-1 example 7:aluminum hydroxy - a G parlor t-butyl benzoate example 8:JIBEN zylidene sorbitol -- an example 9:dimethyl benzylidene sorbitol example 10:screw (2, 4, 8, 10-tetrapod-t-butyl-6-hydroxy-12H-dibenzo [d, g] [1, 3, 2] dioxa-phosphocin-6-oxide) aluminum-hydroxide salt

[0044]

[Table 1]

表　1

		実施例1	実施例2	実施例3	実施例4	実施例5
MFR (g/10分)		2.3	2.3	2.3	2.3	2.3
TREF抽出量 (重量%)		0.6	0.6	0.6	1.5	0.5
分子量分布		5.0	5.0	5.0	5.6	4.9
DSC	融解ピーク温度 (℃)	140.5	140.5	140.5	133.0	145.0
	核剤無添加の結晶化時間 (A) (秒)	217	217	217	484	187
	核剤添加後の結晶化時間 (B) (秒)	15	15	15	15	15
	(A)－(B)	202	202	202	469	172
アンチブロッキング剤	種類	珪酸Mg	珪酸Mg	珪酸Mg	珪酸Mg	珪酸Mg
	平均粒径 (μm)	2.0	2.0	2.0	2.0	2.0
	真球度 (f)	0.90	0.90	0.90	0.90	0.90
	添加量 (重量%)	0.25	0.15	0.50	0.25	0.25
アンチブロッキング剤の脱落		○	○	○	○	○
スクラッチ性		○	○	○	○	○
熱収縮率 (%) (MD+TD)	80℃	10	11	11	18	9
	100℃	21	20	20	28	16
	120℃	45	46	46	52	41
HAZE	収縮前	2.8	1.9	4.0	2.5	3.2
	収縮後	2.9	2.0	4.0	2.5	3.3
GLOSS	収縮前	131	138	121	134	129
	収縮後	130	137	121	134	129
ブロッキング性 (g/10cm²)		300	500	150	400	270
ホットスリップ性	50℃	0.20	0.33	0.05	0.22	0.20
	55℃	0.37	0.47	0.15	0.38	0.33
	60℃	0.77	0.98	0.34	0.89	0.65
溶断シールの耐ピンホール性		○	○	○	○	○

[0045]
[Table 2]

表　2

		比較例1	比較例2	比較例3	比較例4	比較例5
MFR (g/10分)		2.3	2.3	2.3	2.3	2.3
TREF抽出量 (重量%)		0.6	0.6	0.6	0.6	4.0
分子量分布		5.0	5.0	5.0	5.0	5.9
DSC	融解ピーク温度 (℃)	140.5	140.5	140.5	140.5	126.0
	核剤無添加の結晶化時間 (A) (秒)	217	217	217	217	575
	核剤添加後の結晶化時間 (B) (秒)	15	15	15	15	35
	(A)－(B)	202	202	202	202	540
アンチブロッキング剤	種類	珪酸Mg	－	二酸化珪素	PMSO	珪酸Mg
	平均粒径 (μm)	2.0	－	2.0	2.0	2.0
	真球度 (f)	0.55	－	－	0.90	0.90
	添加量 (重量%)	0.25	－	0.25	0.25	0.25
アンチブロッキング剤の脱落		○	－	○	×	○
スクラッチ性		○	○	○	×	×
熱収縮率 (%) (MD+TD)	80℃	10	10	11	10	19
	100℃	22	21	20	21	34
	120℃	46	46	45	47	56
HAZE	収縮前	3.3	1.0	5.0	3.3	2.8
	収縮後	3.3	1.0	4.9	3.2	4.0
GLOSS	収縮前	127	150	117	129	133
	収縮後	127	150	117	129	119
ブロッキング性 (g/10cm²)		400	1,500	200	500	1,300
ホットスリップ性	50℃	0.51	>2.5	0.62	0.22	1.02
	55℃	0.98	>2.5	1.15	0.34	>2.5
	60℃	>2.5	>2.5	>2.5	0.60	>2.5
溶断シールの耐ピンホール性		○	○	○	○	×

珪酸Mg：珪酸マグネシウム　二酸化珪素：不定形の二酸化珪素　PMSO：ポリメチルシルセスキオキサン粒子

[0046]
[Table 3]

表　3

		比較例6	比較例7	比較例8	比較例9	比較例10
MFR (g/10分)		2.3	2.3	2.3	2.3	2.3
TREF抽出量 (重量%)		0.5	5.5	3.9	0.6	0.6
分子量分布		4.9	5.7	7.2	5.0	5.0
DSC	融解ピーク温度 (℃)	152.0	140.5	139.0	140.5	140.5
	核剤無添加の結晶化時間 (A) (秒)	100	297	344	217	297
	核剤添加後の結晶化時間 (B) (秒)	15	15	15	170	無添加
	(A)－(B)	85	282	329	47	－
アンチブロッキング剤	種類	珪酸Mg	珪酸Mg	珪酸Mg	珪酸Mg	珪酸Mg
	平均粒径 (μm)	2.0	2.0	2.0	2.0	2.0
	真球度 (f)	0.90	0.90	0.90	0.90	0.90
	添加量 (重量%)	0.25	0.25	0.25	0.25	0.25
アンチブロッキング剤の脱落		×	○	○	○	○
スクラッチ性		○	×	○	×	×
熱収縮率 (%) (MD+TD)	80℃	7	11	12	12	12
	100℃	13	21	24	21	22
	120℃	37	45	47	45	46
HAZE	収縮前	3.8	3.0	5.2	3.3	3.2
	収縮後	3.9	4.2	5.5	3.7	4.2
GLOSS	収縮前	120	131	114	129	129
	収縮後	120	119	112	120	117
ブロッキング性 (g/10cm²)		200	350	250	400	400
ホットスリップ性	50℃	0.19	0.21	0.21	0.23	0.20
	55℃	0.35	0.59	0.40	0.50	0.41
	60℃	0.65	0.92	0.78	0.95	0.90
溶断シールの耐ピンホール性		○	△	○	×	×

珪酸Mg：珪酸マグネシウム

[0047]
[Table 4]
表　4

		実施例6	実施例7	実施例8	実施例9	実施例10
MFR (g/10分)		2.3	2.3	2.3	2.3	2.3
TREF抽出量 (重量%)		0.6	0.6	0.6	0.6	0.6
分子量分布		5.0	5.0	5.0	5.0	5.0
DSC	融解ピーク温度 (℃)	140.5	140.5	140.5	140.5	140.5
	核剤無添加の結晶化時間 (A) (秒)	217	217	217	217	217
	核剤添加後の結晶化時間 (B) (秒)	15	15	15	15	15
	(A)－(B)	202	202	202	202	202
アンチブロッキング剤	種類	珪酸Mg	珪酸Mg	珪酸Mg	珪酸Mg	珪酸Mg
	平均粒径 (μm)	2.0	2.0	2.0	2.0	2.0
	真球度 (f)	0.90	0.90	0.90	0.90	0.90
	添加量 (重量%)	0.25	0.25	0.25	0.25	0.25
アンチブロッキング剤の脱落		○	○	○	○	○
スクラッチ性		○	○	○	○	○
熱収縮率 (%) (MD+TD)	80℃	10	11	11	10	12
	100℃	20	22	21	20	22
	120℃	45	46	46	46	45
HAZE	収縮前	2.9	2.9	2.9	2.8	2.8
	収縮後	3.0	3.0	3.0	3.0	2.9
GLOSS	収縮前	130	130	129	131	130
	収縮後	129	129	129	130	129
ブロッキング性 (g/10cm²)		280	300	300	300	270
ホットスリップ性	50℃	0.20	0.20	0.19	0.21	0.21
	55℃	0.35	0.36	0.37	0.35	0.37
	60℃	0.78	0.78	0.79	0.77	0.76
溶断シールの耐ピンホール性		○	○	○	○	○

[0048]
[Effect of the Invention] The film for shrink packages obtained by the method of this invention, By blending a specific nucleating additive and a specific specific anti blocking agent with a specific propylene system resin, low-temperature shrinkage characteristics are excellent, and it excels in transparency, gloss, a blocking resistance, and scratch nature, and, moreover, excels in the hot slip nature at the time of packing, and the pinhole-proof nature at the time of the shrink package behind a fusing seal, there are few falls of the transparency after contraction and gloss, and it is the film which does not have defluxion of an anti blocking agent at the time Taking advantage of this outstanding property, it has practical value very high as a film for shrink packages.

[Translation done.]

PAT-NO: JP405309732A

DOCUMENT-IDENTIFIER: JP 05309732 A

TITLE: FILM FOR HEAT RESISTANT SHRINK LABEL

PUBN-DATE: November 22, 1993

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APPL-NO: JP04145017

APPL-DATE: May 12, 1992

INT-CL (IPC): B29C061/06, B29C047/14 , B29C055/04 , C08J005/18 , C08L023/16 , G09F003/04

US-CL-CURRENT: 425/66

ABSTRACT:

PURPOSE: To obtain a film for a shrink label which is excellent in close fast adhesion to a container in shrink packaging and can sufficiently withstand high temperature pasteurization treatment.

CONSTITUTION: A resin composition wherein principal components are 80-30wt.%

of crystalline propylene.-ethylene random copolymer of 140-160°C in melting point, 10-60wt.% of propylene monopolymer of M11-10, and 2-15wt.% of petroleum resin of 115-140°C in softening temperature, and a main peak of a crystal fusion curve by DSC is 150-160°C, is fusion extruded and quickly cooled to obtain an actually non-oriented raw film. The raw film is streched 3.0-7.0 times uniaxially within a temperature range of 100-140°C.

* NOTICES *

1. This document has been translated by computer.So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] Especially this invention relates to the film for heat-resistant shrink labels which has useful retort aptitude in the drinks (coffee etc.) for which it excels in transparency in more detail, and contents need pasteurization processing especially about the film for shrink labels used for covering protection and the outside ornament of a glass bottle.
[0002]
[Description of the Prior Art] The polyvinyl chloride film, the polystyrene film, etc. are used as a conventional film for shrink labels. However, these films were lacking in thermal resistance, and were not what can be equal to pasteurization processing. On the other hand, although the resin of a high-melting point is used in order to obtain good thermal resistance in the film for shrink labels of a polyolefine system, especially a polypropylene system, shrinkage characteristics become inadequate and the adhesion at the time of carrying out a shrink package to a container becomes bad. Moreover, although the resin of comparatively the low melting point, for example, an ethylene-propylene random copolymer with a high ethylene content, the ethylene-propylene-alpha olefin ternary polymerization object, etc. are used in order to obtain good contraction workmanship nature, there is a point inadequate for thermal resistance.
[0003]
[Problem(s) to be Solved by the Invention] this invention satisfies the above opposite properties, namely, its adhesion to the container in a shrink package is good, and it offers the film for shrink labels which can be equal also to pasteurization processing enough.
[0004]
[Means for Solving the Problem] In order for the skin temperature of the film when coming out of a shrink tunnel to be before and after 80 degrees C for example, film temperature is lower than it, and for the usual contraction conditions to be clearly insufficient [the skin temperature] in contraction in the case of 70 degrees C, as a result of examining many things, in order that this inventions may solve the aforementioned trouble, and to be higher than it in film temperature, for example, to make it 90 degrees C. It is necessary to raise the preheat temperature of a ** glass bottle too much, to make shrink tunnel temperature high sharply again, or to lengthen pass time of a shrink tunnel. However, it is the thing and bird clapper which are not desirable as practical shrink-package conditions making all clear, and observing a shrink-package workmanship situation finely further. difference [of the contraction stress value at the time of heating in the thermal-contraction stress whose adhesion of the label by which the shrink package was carried out on the conditions from which film temperature becomes 80 degrees C is 80 degrees C (A), and the contraction stress value at the time of after / heating / air cooling (B)] (A) - it found out that there were (B) and a good correlation That is, it turns out that (Difference A)-(B) of a thermal-contraction stress value is low, and what has the good adhesion of a label is 2 15g/mm especially. The following finds out a good thing and reaches this invention. That is, this invention has

the main peak temperature of a DSC crystal dissolution peak in 150 degrees C - 160 degrees C, and the rate of a thermal contraction in 120 degrees C is 25% or more in the extension direction. And it sets in thermal-contraction stress of 80 degrees C, and the contraction stress value at the time of heating ((Difference A)-(B of the contraction stress value at the time of A) and after [heating] air cooling (B)) is 2 15g/mm. Film for heat-resistant shrink labels with good adhesion characterized by being the following. And 80 - 30 % of the weight of crystalline propylene-ethylene random copolymers whose melting point is 140-160 degrees C, and MI should make a principal component 2 - 15 % of the weight of petroleum resins whose 10 - 60 % of the weight of propylene homopolymers and softening temperature of 1-10 are 115-140 degrees C, and should carry out melting extrusion of the resin constituent whose main peak of the crystal melting curve by DSC is 150-160 degrees C. It is related with the manufacture method of a heat-resistant shrink label that the aforementioned adhesion characterized by the thing which quenched, and for which the original fabric film of non-orientation is substantially extended 3.0 to 7.0 times to 1 shaft orientations by the 100-140-degree C temperature requirement was excellent.

[0005] this invention is explained in detail below. the crystalline propylene-ethylene random copolymer used in this invention -- the melting point -- 140 degrees C - 160 degrees C -- desirable -- a 145 degrees C - 155 degrees C thing -- desirable -- usually -- an ethylene content -- 2 - 10% of the weight of a thing -- it is 2 - 5% of the weight of a thing still more preferably Since the shrinkage characteristics of the film which will be obtained if that to which the white blush mark of a film and blocking of labels take place, and the melting point exceeds 160 degrees C is used when thermal resistance falls and the melting point carries out pasteurization processing at less than 140 degrees C run short and about [that the adhesion to a container becomes bad] or heat-sealing nature also gets worse, neither is desirable. The thing for 1-10g / 10 minutes is used for MI, and, as for the propylene homopolymer used by this invention, the thing of 1.5-7 is used more suitably further. Since MI of melt viscosity is too high, regulation of extrusion film production is difficult, and when MI exceeds 10, melt viscosity is too low, thickness adjustment is difficult for less than one thing, and its neither is practical. Moreover, the adhesion to the container of the shrink label with which the loadings of a propylene homopolymer are obtained at less than 10 % of the weight is inadequate, and a retort property is still more inadequate. When it exceeds 60 % of the weight, **** of the label after a shrink package does not become uniform, but appearance changes with bad packaging goods. Although a petroleum resin, a hydrogenation petroleum resin, a terpene resin, a hydrogenation terpene resin, etc. are mentioned and ARUKON P-115 made from Arakawa Chemical industry, P-125, P-140, FURIARON P-115 made from Yasuhara Resin Industry, P-125, and the S KORETTSU 5320 grade made from Exon Chemistry are specifically mentioned among commercial goods as petroleum resins in this invention, it is not limited to these. That whose softening temperature is 115 degrees C - 140 degrees C especially is used suitably. Such a petroleum resin is added two to 15% of the weight to a total constituent weight. The crystallinity of a constituent becomes high and less than 2 % of the weight of ductility, transparency, thermal-contraction nature, and heat-sealing nature is insufficient, and since a white blush mark will arise on the film of retorting ** or it will become easy to carry out blocking to it if it exceeds 15 % of the weight conversely, it is not desirable.

[0006] The film for shrink labels in this invention, A principal component consists of 80 - 30 % of the weight, 10 - 60 % of the weight, and 2 - 15 % of the weight in a crystalline propylene-ethylene random copolymer, a propylene homopolymer, and petroleum resins, respectively, and the main peak of the crystal melting curve by DSC extends the original fabric film of non-orientation 3.0 to 7.0 times to 1 shaft orientations by the 100-140-degree C temperature requirement, and is acquired by the real target which did melting extrusion of the resin constituent which is 150-160 degrees C, and quenched it. The main peak temperature by DSC of the above-mentioned constituent becomes inadequate [thermal resistance] for it to be less than 150 degrees C, and when pasteurization processing is carried out, neither the white blush mark of a film nor blocking of labels happens and is desirable. Moreover, if main peak temperature exceeds 160 degrees C, when it becomes inadequate [shrinkage characteristics] although thermal resistance became good, and the shrink package of the container is carried out,

adhesion of a shoulder and a bottom will be inadequate and appearance will become bad. In addition, in the mixed resin constituent used by this invention, an antioxidant, an antistatic agent, an ultraviolet ray absorbent, and the additive of lubricant and others can be included if needed. The extrusion temperature in the process which carries out melting extrusion of the above-mentioned constituent has desirable 300 degrees C or less, and its temperature while being 160 degrees C - 280 degrees C is still more desirable. if an extrusion temperature exceeds 300 degrees C -- a propylene system polymerization -- since the petroleum resins mixed in the inside of the body cause a pyrolysis and generating, remarkable emitting smoke, etc. of air bubbles arise, it is not desirable The film by which melting extrusion was carried out from the flat die of an extruder is quenched before crystallization progresses, and it obtains a non-extended original fabric film substantially. The film which is not extended on the obtained real target is extended 3.0 times to 7.0 times to 1 shaft orientations at the temperature of 100 degrees C - 140 degrees C. In this case, extension with extension temperature uniform at less than 100 degrees C cannot be performed, but extension nonuniformity occurs or problems, like natural contraction of the obtained film is large arise. Conversely, since the trouble on the process of a film adhering to an extension roll will occur or a fault, like the low-temperature shrinkage characteristics of the film obtained are inferior will arise if extension temperature exceeds 140 degrees C, neither of the cases is desirable. Moreover, in less than 3.0 times, the orientation to the extension direction has small draw magnification, and looseness arises at the time of pasteurization processing. Moreover, if 7.0 times are exceeded, shrinkage characteristics will fall conversely and the adhesion to a container will become bad. Thus, some thing of the obtained film to do for relaxing heat processing is desirable in order to suppress natural contraction. Although 60 degrees C - 100 degrees C and heat treatment time are suitably set for heat treatment temperature according to heat treatment temperature, the short processing time is used as heat treatment temperature becomes high. Known surface treatment, such as a corona treatment, can be performed on a front face, and printing and metal vacuum evaporationo processing can be carried out to the film obtained as mentioned above if needed.

[0007] The rate of a thermal contraction of 120 degrees C obtained as mentioned above is 25% or more, and stops the contraction stress value at the time of heating (A), and heating at 80 degrees C at 80 degrees C. The thermal-contraction stress value ((Difference A)-(B of B)) immediately after starting air cooling is 2 15g/mm. When the shrink package of the film for shrink labels in this invention which is the following is usually carried out with a shrink tunnel, a label can stick it to a container and it can obtain packaging goods excellent in appearance. The difference of a thermal-contraction stress value in case after [heating] air cooling is carried out to the thermal-contraction stress when adhesion being inadequate when a shrink package is carried out to the rate of a thermal contraction being less than 25% to a container, and being heated by 80 degrees C is 2 15g/mm. Since the fall of the contraction stress at the time of cooling is large when it exceeds. Adhesion cannot become inadequate, packaging goods excellent in appearance cannot be obtained, and the purpose of this invention must have been attained.

[0008]

[Example] Next, although an example explains this invention concretely, this invention is not limited to these. In addition, the measuring method of the error criterion of the label property in this invention and the rate of a thermal contraction, and thermal-contraction stress is as follows.

(1) The cylinder-like sleeve was created, as the film was cut off to label property 97mm long (it is the right-angled direction to the extension direction), and 180mm (the extension direction) wide and edges overlapped 5mm by impulse heat sealing in edges parallel to lengthwise. After equipping a bottle with this sleeve so that it may be protected from the bottle shoulder of 180ml glass bottle with a height [of 130mm], and a diameter [of a drum section] of 54mm to a bottom, the glass bottle which the 280-degree C hot blast formula shrink tunnel was made to carry out the thermal contraction of through one and the oriented film, and carried out labeling to it for 4 seconds was obtained. The following method estimated this glass bottle that carried out labeling.

[adhesion] -- the time of pressing down by hand after a thermal contraction, so that a film may be wrapped, and turning a glass bottle to a circumferencial direction -- the surroundings -- being hard -- it is

-- it is -- O mark showed that around which it does not turn at all, and x mark showed that around which it turns lightly
[Appearance] It judged in the state of adhesion with a film and a glass bottle after the thermal contraction, O mark completely showed Siwa, the crater, and the thing without a bite lump of air, and x mark showed ** mark, Siwa, and what has many craters for what Siwa and a crater are partially regarded as.
[Homogeneity of label **** of a bottle shoulder] **** of a label showed what generating of O mark, the thing which lenticulated, and Siwa was regarded as in the straight-line-like thing by x mark mostly.
[Retort aptitude] The appearance when taking out the glass bottle which carried out labeling after 130 degrees C and 30-minute pressurization hot water processing was judged. It loosened, O mark, the partial thing which the white blush mark etc. has produced, and the front face that which is completely changeless processing before, and x mark showed the bad thing of adhesion. [the BETO **** thing and the whole target]
(2) Cut off a sample film so that it may become the square of about 100mm in the rate extension direction of a thermal contraction, and it and the right-angled direction, and it is full size:L0. (mm) is read. It is immersed for 10 seconds during the glycerol bath controlled by 120 degrees C **0.5 degrees C, and water cooling of this cut-off sample is carried out promptly after that.
Size:[of the extension direction of a sample] L (mm) which carried out heating contraction was read, and the rate of a thermal contraction of a formula 1 was computed.
(3) From a thermal-contraction stress film, sample in the size of 10mm in 50mm, it, and the right-angled direction in the extension direction, and set a sample in a thermal-contraction stress measuring device. Next, a sample is heated by being immersed for 5 seconds in 80-degree C hot water, and the contraction stress curve when stopping being immersed immediately subsequently and starting air cooling is recorded on a recorder. The stress value immediately after (A) and an air-cooling start was set to (B) for the maximum-stress value at the time of heating for 5 seconds.
[0009]
[Formula 1]

$$\text{熱収縮率 (\%)} = \frac{L_0 - L}{L_0} \times 100$$

[0010] 75 % of the weight (146 degrees C of melting points) of example 1 crystallinity propylene-ethylene random copolymers, 20 % of the weight (168 degrees C of melting points) of propylene homopolymers, and 5 % of the weight (softening temperature of 125 degrees C) of petroleum resins were kneaded with the 2 shaft kneading extruder, and pellet-like mixture was obtained. Melting kneading of this mixture was carried out at 170 degrees C - 260 degrees C, and from the T die kept at 230 degrees C, it extruded in the shape of a sheet, and cooled to 25 degrees C by the cooling roller. This unstretched film was heated to 125 degrees C, and it extended 3.5 times to lengthwise by the roll drawing machine. Subsequently, relaxing heat processing was performed for this oriented film for 5 seconds through the 75-degree C hot calender roll. The thickness of the obtained oriented film was 100 micrometers. A result is shown in Table 1. the difference (A) of the thermal-contraction stress value whose rates of a thermal contraction whose main peak temperature of a DSC crystal dissolution peak of the obtained film is 153 degrees C and 120 degrees C are 35% and 80 degrees C so that the result of Table 1 may show - (B) -- 15g/mm2 it was . Next, it was the film for shrink labels which is excellent in the homogeneity of adhesion, appearance, and label ****, and retort aptitude, and can bear this film also at pasteurization processing as a result of evaluating in accordance with the error criterion of a label property.
[0011] 50 % of the weight (146 degrees C of melting points) of example 2 crystallinity propylene-ethylene random copolymers, 40 % of the weight (168 degrees C of melting points) of propylene homopolymers, and 10 % of the weight (softening temperature of 125 degrees C) of petroleum

resins were kneaded with the 2 shaft kneading extruder, and pellet-like mixture was obtained. The oriented film with a thickness of 100 micrometers was obtained like the example 1 except having increased draw magnification 3.6 times. A result is shown in Table 1. the difference (A) of the thermal-contraction stress value whose rates of a thermal contraction whose main peak temperature of a DSC crystal dissolution peak of the film obtained so that the result of Table 1 might show is 155 degrees C and 120 degrees C are 33% and 80 degrees C - (B) -- 8g/mm2 it was . As a result of evaluating a label property like an example 1, it excelled in the homogeneity of adhesion, appearance, and label ****, and retort aptitude, and was the film for shrink labels which can be equal also to pasteurization processing.
[0012] The oriented film with a thickness of 100 micrometers was obtained like the example 1 except changing an example 3, 4 raw-material composition, extension temperature, and draw magnification, as shown in Table 1. A result is shown in Table 1. It was what has the property which was excellent like examples 1 and 2 so that the result of Table 1 might show.
[0013] Like the example 1, the film was extrusion-produced, 100 % of the weight of example of comparison 1 crystallinity propylene-ethylene random-copolymer (146 degrees C of melting points) pellets was extended, and the oriented film with a thickness of 100 micrometers was obtained. A result is shown in Table 1. since there is no addition of a propylene homopolymer -- a difference with a thermal-contraction stress value of 80 degrees C -- 4g/mm2 it is -- although -- about [that the peak temperature of a DSC crystal dissolution peak becomes are 146 degrees C and inadequate / retort aptitude], or adhesion mist -- it was inadequate
[0014] The oriented film with a thickness of 100 micrometers was obtained like the example 1 except having changed draw magnification 2.0 times by raw material composition of example of comparison 2 example 3. A result is shown in Table 1. The difference of 80-degree-C thermal-contraction stress value is 2 30g/mm so that the result of Table 1 may show. It became, milkiness and looseness arose in about [that adhesion becomes inadequate] and retorting, and it was unsuitable as a film for heat-resistant shrink labels.
[0015] The 100-micrometer oriented film was obtained like the example 1 except having made it raw material composition of 10 % of the weight of example of comparison 3 crystallinity propylene-ethylene random copolymers, 80 % of the weight of propylene homopolymers, and 10 % of the weight of petroleum resins. A result is shown in Table 1. Since the rate of a thermal contraction of 120 degrees C was 23% as the result of Table 1 showed, the appearance of a label and the homogeneity of **** were inadequate, and it was unsuitable as a film for shrink labels.
[0016] The 100-micrometer oriented film was obtained like the example 1 except having changed extension temperature into 145 degrees C by raw material composition of example of comparison 4 example 3. A result is shown in Table 1. The rate of a thermal contraction of 120 degrees C was 15%, and the homogeneity of the adhesion of a label, appearance, and **** was inadequate so that the result of Table 1 might show. The adhesion to a container and label appearance are also good, and, as for the film for shrink labels obtained by this invention, the above result shows that it is the film for shrink labels which has the outstanding property which can be equal also to pasteurization processing enough.
[0017]
[Table 1]

		実施例				比較例			
		1	2	3	4	1	2	3	4
原料組成	プロピレンーエチレンランダム共重合体（wt%）	75	50	40	40	100	40	10	40
	プロピレン単独重合体（wt%）	20	40	50	50	0	50	80	50
	石油樹脂類（wt%）	5	10	10	10	0	10	10	10
混合組成物DSC融解メインピーク（℃）		153	155	157	158	146	157	163	157
延伸条件	延伸温度（℃）	125	125	120	125	125	125	125	145
	延伸倍率（倍）	3.5	3.6	3.5	4.0	4.0	2.0	3.5	3.5
フィルム 延伸 ラベル特性	密着性	○	○	○	○	○△	○	○	×
	外観	○	○	○	○	△	○	×	×
	縦肩部のラベル縮線の均一性	○	○	○	○	○	○	×	×
	レトルト適性	○	○	○	○	×	×	○	−
フィルム 熱収縮率（%）（120℃）		35	33	29	30	40	40	23	15
フィルム 収縮応力（g/mm²） 熱	加熱時（A）	130	160	186	200	117	180	180	45
	加熱後空冷時（B）	115	152	185	200	113	150	200	40
	（A）−（B）	15	8	1	0	4	30	−20	5

[0018]

[Effect of the Invention] Although a shrink tunnel is usually used when carrying out the shrink package of the label to a container When the shrink label was used for the container as the rate of a thermal contraction is less than 25%, and a shrink package is carried out, The difference of the thermal-contraction stress value immediately after the air-cooling start after coming out with the thermal-contraction stress when adhesion becoming inadequate, and a label shrink tunneling and being heated is 2 15g/mm. Although adhesion will become inadequate since the fall of contraction stress is large if it exceeds Its adhesion to the container by the shrink package is good, and since the film obtained by this invention is excellent in transparency and can be equal also to pasteurization processing enough, it is especially useful as films for shrink labels, such as canned and a coffee drink containing a bottle.

[Translation done.]